Chemistry I

Kinetic Molecular Theory

Introduction

- Is a model of matter used to explain matter and states of matter.

Kinetic Molecular Theory

- Three points:
- 1. All matter is made of tiny particles.
- 2. These particles are in constant motion.
- 3. The total kinetic energy of the colliding particles remains constant.

Kinetic Energy

The energy of motion.

Calculated by:

$$K.E. = \frac{1}{2}\, m\, (v^2)$$

Where m is mass in kg and v is velocity (speed) in m/s.

Forces between molecules

- Attractive forces exist between ALL molecules. These are called van der Waals forces and come under two classifications:
  - 1. Dispersion interaction forces for all molecules.
  - 2. Dipole-dipole attraction which exist for polar molecules only.

Molecules and dipoles

- Most covalent compounds do have a polar nature.
- A dipole is a molecule which has a distinct separation of charge even though there is a sharing of e^{-1}s (covalency), like HCl

$$\underset{\delta+}{H}\text{—}\underset{\delta-}{Cl}$$

Solids: Basic Information

- Definite shape : maintains its shape; does not flow
- Definite volume (all surfaces are free)
- Solid cannot be compressed
- Solids diffuse (extremely slowly)

Characteristics of solids

- Particles are very close together.
- Particles vibrate in place.
- Particles have very very low kinetic energy.
- Force of attraction between particles is very strong.

Solids and KMT

- 1. Tiny particles are held very close together in fixed positions with strong forces.
  - If in regular alignment- crystalline
  - If not in regular alignment – amorphous
- 2. Kinetic energy of particles results from their vibrating around their fixed position. Temperature is a measure of their motion; higher temperature means more kinetic energy.

Solids and KMT

- 3. Because particles have fixed positions; there is very little diffusion.
- 4. Because particles are so close, they cannot be compressed(pushed any closer together).

Solids as crystals

- Crystalline
  - Crystal-highly organized regular geometric pattern (arrangement)
    - Ex: any crystal
  - Amorphous-random particle arrangement
    - Ex: glass or wax
  - Note: the 7 different types of geometric patterns have been defined by x-ray diffraction techniques

Crystals and binding forces

- If molecules are nonpolar, then the binding forces are weak.
- If the molecules are polar, then the binding forces are stronger through dipole-dipole forces and dispersion interaction forces (van der Waal forces)

4 general categories of crystals

- 1. Ionic crystal
- 2. Covalent network
- 3. Metallic crystal
- 4. Covalent molecular crystal

Crystal types and characteristics

1. **Ionic Crystals** are an array of positive and negative ions. The strong binding forces are between the anions and the cations. These forces are electrostatic in nature. The elements in Groups 1,2,6 and 7 along with the radicals form this type of crystal, which are hard and brittle with high melting points. They are also poor conductors of heat and electricity.

- Example: halite ($NaCl$), calcite ($CaCO_3$)

Crystal types and characteristics

2. **Covalent Network Crystals** Each atom sharing electrons with neighboring atoms in the crystal holds crystal together.

   The binding forces are strong covalent bonds. These crystals are very hard and brittle with high melting points and are nonconductors. These crystals can be thought of a one big molecule!!!!!

- Examples: diamonds, silicon dioxide

Crystal types and characteristics

3. **Metallic Crystals** are formed by positive ions (metal) surrounded by a cloud of electrons that flow freely between the atoms. The binding force are between the positive metals ions and the *electron cloud*. These crystals exhibit variable hardness (soft to hard), variable high melting point, and are all conductor of electricity. These crystals show high density values.

- Example: any metal

Crystal types and characteristics

4. Covalent Molecular Crystals (also called molecular crystals) have an orderly array of distinct molecular units. (Molecules are the building blocks). These compounds are soft with low melting points and are poor conductors. The forces holding these crystals together are interactions between molecules like van der Waals forces and hydrogen bonding.

- Example: sugar crystals

Solids and change of state

- Solids can change from solid to liquid and even to a gas
- Some solids can jump from a solid to a gas or a gas to a solid.
- The term given to this change of state.
- Energy is involved in this process.

Solids and change of state

- Definition: molar heat of fusion: the energy needed to melt one mole of solid at its m.p.
- Note: a solid can go from solid to liquid to gas and a dynamic equilibrium can be reached with melting and freezing
- Solids like CO_2 & I_2 and naphthalene go directly from solid $\longrightarrow$ vapor.This is called sublimation. They have high equilibrium vapor pressure.

Solids and change of state

- To change a solids state:
  - Liquid – energy $\longrightarrow$ solid (freezing)

    or
  - Liquid $\longrightarrow$ solid + energy (melting)

  - For pure solids, the m.p. and f.p. are the same.

Liquids: Basic Information

- Five characteristics:
  - 1. Definite volume (one free surface; takes shape of container)
  - 2. Fluidity (can flow or be poured) a measure of this is called viscosity.
  - 3. Noncompressibility (compressed very little by applied pressure)
  - 4. Diffusion – ability to spread throughout each other(liquids mix)
  - 5. Evaporation – ability to go into vapor state even at room temperature.

Characteristics of Liquids

- Particles are close together.
- Particles move around each other(flow).
- Particles have a fair amount of kinetic energy.
- Force of attraction between particles is strong.

liquids and KMT

- Attractive forces between liquid particles are strong enough so that liquid has a definite volume but weak enough so they can move.
- there is enough kinetic energy to allow this motion.

liquid characteristics

- substances of low molecular weights and nonpolar molecules are liquids only **below** room temperature (r.t = 20^{o}C)
- Substances with higher molecular weights and nonpolar molecules can **be** at r.t.
- Substances of low molecular weight and polar molecules (like water) may be liquid at r.t. reason is a stronger combination of van der Waal forces.

Physical Properties of Liquids

- Boiling
  - Defined: the boiling point of a liquid is the temperature at which the equilibrium vapor pressure of the liquid is equal to the atmospheric pressure(pressure on the weather channel).
- Applied pressure: Pascal's Law
  - The pressure on a liquid in a confined container is distributed evenly in all directions.

Evaporation

- Evaporation happens when some molecules acquire enough kinetic energy to escape from liquid surface and go into vapor phase. (have over come attractive forces)
- Vapor is the gas of a material which is usually a liquid or solid at r.t.
- These vapor molecules also exert a pressure which depends on temperature and types of liquid or solid.

What happens in boiling liquids

- 1. When boiling begins:
  - Vapor bubbles rise from the bottom (where it’s hottest).
  - If the vapor pressure on the liquids surface is not yet equal to atmospheric pressure, the bubble collapses.

What happens in boiling liquids

- 2. As temperature of the liquid increases vapor pressure increases.
  - Finally a temperature is reached where equilibrium vapor pressure is equal to atmospheric pressure.
- 3. Now, Vapor bubbles rise to the surface, evaporation occurs readily BUT the liquid will not increase in temperature. It is at its boiling point(b.p.). Boiling points listed in literature are adjusted to standard pressure.

Does atmospheric pressure affect b.p.?

- Once boiling occurs, the temperature does not change.
- Note: temperature of vapor at boiling is the same as the liquid. Heat must be supplied continually. Remember, extra energy needed to overcome attractive forces between liquid molecules to go into wider spacing of vapor molecules.

Does atmospheric pressure affect b.p.?

- 1. High pressure will produce a higher b.p.
  - Higher vapor pressure
  - More energy needed to get molecules to escape.
- 2. Low pressure will lower the b.p.
  - Lower vapor pressure
  - Less energy needed to get molecules to escape.
  - Think of boiling stuff in Denver, CO.

Standard Heat of Vaporization

- Definition: the heat energy required to vaporize 1 mole of a liquid at its standard boiling point .
- What does it depend on?
  – The attractive forces between molecules.

Basic Information on Gasses

- Particles are far apart.
- Particles have large amount of kinetic energy.
- Particles collide with each other.
- Force of attraction between particles is very, very weak.

Characteristics of Gases

- 4 characteristics:
  - 1. Expansion (volume chances)
  - 2. Pressure (exerted on and by them)
  - 3. Low density (in g/L)
  - 4. diffusion

KMT and Gasses

- Gasses have a large amount of energy compared to solids are therefore the particles are moving quite rapidly
- These molecules are in random motion and collide with each other.
- Because the particles (atoms or molecules) are far apart the forces of attraction are very weak

Liquefying gases

- Converting a material that is normally a gas at r.t. to become a liquid.
- This operation involves two steps which are continually repeated:
  - 1. Compressing the gas; applying pressure
  - 2. Allowing gas to re-expand

* what happens to the temperature of a gas if the pressure is increased ?

- Applying the combined gas law with both volumes constant so p and T will vary directly.
- Why? If work is done on molecules to push them closer together, they absorb energy from this kinetic energy applied to them. They show it in the *form* of increased temperature.

The Process looks like this.

- So, we
  - 1. Compress gas molecules
  - 2. They come closer together
  - 3. Extra heat energy is removed by a coolant
  - 4. The gas molecules are allowed, at its starting temperature, to re-expand to original volume. *in re-expanding, the gas loses energy. So, it is at the same volume but at lower temperature.

The Process(cont’d)

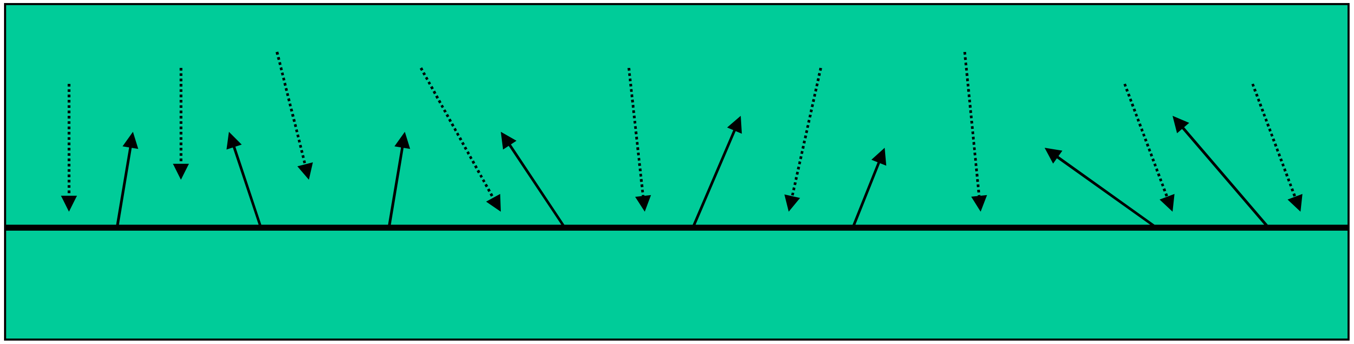
- The procedure is repeated:
  - 1. Compression is again applied
  - 2. Extra absorbed energy is removed
  - 3. In re-expanding, the gas loses more energy(cooler).
- What’s happening? The lowered temperature slows molecular movement. The increased pressure crowds molecules together. Eventually, attractive forces cause the gases to condense onto liquid form.

Dynamic Equilibrium

- Generally speaking this means that things are changing and the two processes are equal but opposite.
- Take the case of evaporation: the number of molecules that are going into the vapor state is equal to the number of molecules returning to (condensing) the liquid state.

Dynamic Equilibrium

- Closed container with liquid at a constant temperature.



Dynamic Equilibrium

- Eventually, the number of vapor molecules condensing will equal the liquid molecules evaporating.
- There is no net change; there is an equilibrium.
- However, the evaporation and condensation don’t stop! It is the rates that are equal. The rates are at equilibrium.

Dynamic Equilibrium

- It is called a dynamic condition because 2 opposing changes are happening at equal rates.
- They can be shown in equation form:
  - Evaporation: liquid + energy $\longrightarrow$ vapor
  - Condensation: vapor – energy $\longrightarrow$ liquid

    or vapor $\longrightarrow$ liquid + energy

Dynamic Equilibrium

- Finally combining the last two equations:
  - Liquid + energy $\longleftrightarrow$ vapor
    - Or $\rightleftharpoons$

Equilibrium vapor pressure

- When this condition exists, a vapor hangs over top of the liquid. This creates an equilibrium vapor pressure. This pressure is particular to the liquid and is temperature dependent.
- By definition: equilibrium vapor pressure is the pressure exerted by a vapor in equilibrium with its liquid.

Disturbance in the equilibrium

- What will happen if the temperature of a liquid is increased?
    - More energy is added to the system
    - The molecules will move faster
    - More liquid will evaporate
- This will upset the equilibrium.
- If a higher temperature is maintained then a new equilibrium point will be established with an increase in vapor pressure(more vapor above liquid surface with more push).

Disturbance in the equilibrium

- Equilibrium vapor pressure depends on:
  - Temperature
  - Attractive forces between liquid molecules
  - Note: if forces are strong;molecules will keep together causing the vapor pressure to be lower.

So what happens when……

- If:
  - A. increase (or decrease) temperature, the vapor-liquid equilibrium is upset.
  - B. an upset causes a stress on the system
  - C. a stress to one rate (forward or backward) upsets the equilibrium(knocks it out of wack)
  - D. it is possible to shift the equilibrium in a desired direction.

Le Châtelier's Principle

- Was formulated in 1888 and says:
  - If a system at equilibrium is subjected to a stress(upset), the equilibrium will be displaced (shifted) in such a direction as to relieve the stress.
  - This applies to ALL types of dynamic equilibrium.

Le Châtelier's Principle and liquid-vapor systems

- 1. if temperature is raised: more energy;molecules moving faster,more molecules into vapor state; higher vapor pressure: new equilibrium established
- 2. If temperature is lowered: less energy;molecules moving slower; fewer molecules in vapor state;new equilibrium with lower vapor pressure.

Critical Temperature and Pressure

- Gases have a certain temperature and a certain pressure at which they will liquefy.
- Definition: critical temperature: the highest temperature at which it is possible to liquefy a gas with any amount of pressure
- Definition: critical pressure: the pressure required to liquefy a gas at its critical temperature.

Critical Temperature and Pressure(cont'd)

- Definition: critical volume: the volume occupied by 1 mole of a gas at its critical temperature and critical pressure.
- Let's say it this way: critical temperature is the temperature above which a gas cannot be liquefied no matter how much pressure is applied.

Critical temperature and attractive forces

- There is a relationship between critical temperature and attractive forces.
  - The higher the critical temperature, the greater the attractive forces once the gas has become a liquid.
  - The lower the critical temperature, the weaker the attractive forces.
  - Example: water vapor has a high critical temperature, and water has much attraction in its polar structure.

Critical temperature and attractive forces

- Nonpolar covalent molecules like O_2 , N_2 and H_2 do have attractive forces, but they are weak dispersion (van der Waal) forces.
- General Rule: higher critical temperature usually means higher attractive forces in liquid molecules and usually a greater molecular weight.

Water

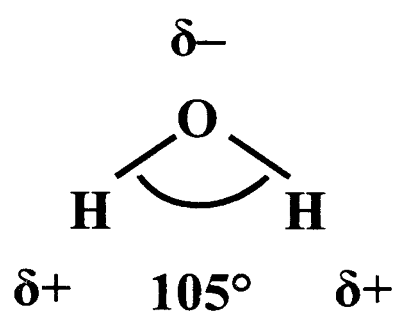
- Physical properties of dihydrogen monoxide
  - Transparent
  - Odorless
  - Colorless
  - Tasteless
  - f.p. = $0^{o}C$ @ standard pressure
  - b.p. = $100^{o}C$ @ standard pressure

Special Property of water

- Water does some really weird thing we it cools down. Like most substances, it contracts (particles move closer) as it cools. BUT at 4^{o}C, water begins to expand (increase in volume and becomes less dense). As it forms ice, it has expanded more and is less dense; that’s why ice floats in water. Water reaches its maximum density at 3.98^{o}C (1.0000 g/mL)

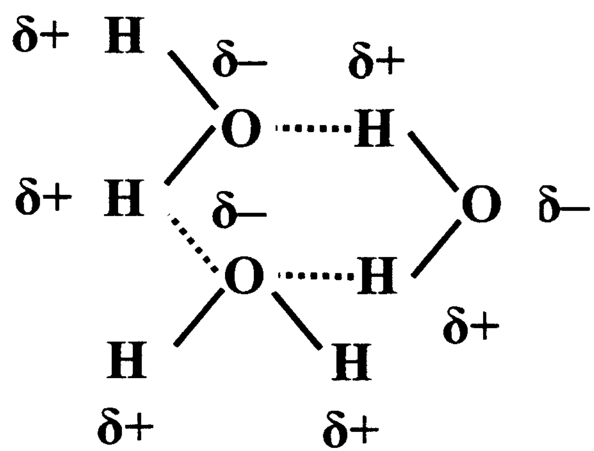
Water molecule

Water molecule showing dipoles & bond angle



Water dipoles and association

- Diagram of polarity and hydrogen bonding in water molecules.



Hydrogen bonding

- Hydrogen bonding is weak chemical bonding between a hydrogen atom in one polar molecule and a very electronegative atom in a second polar molecule.
- Hydrogen bonding in water accounts for:
  - 1. Water being a liquid at r.t.
  - 2. The hexagonal crystal structure of ice (water molecules in hexagonal rings together)

Hydrogen bonding

- Hydrogen bonding is confined to hydrogen and small electronegative atoms such as oxygen, fluorine, and nitrogen.(this is why NH_3 has a high critical temperature and is used as a refrigerant.)

Ice

- Melting ice: when heated, hydrogen bonds stretch because they are flexible. Groups of molecules in liquid form are more compact than groups of molecules in solid form(ice) where they are in fixed positions. (same # of molecules of ice have more volume than same # of molecules of liquid water) ice is less dense than cold water so it floats!!!!

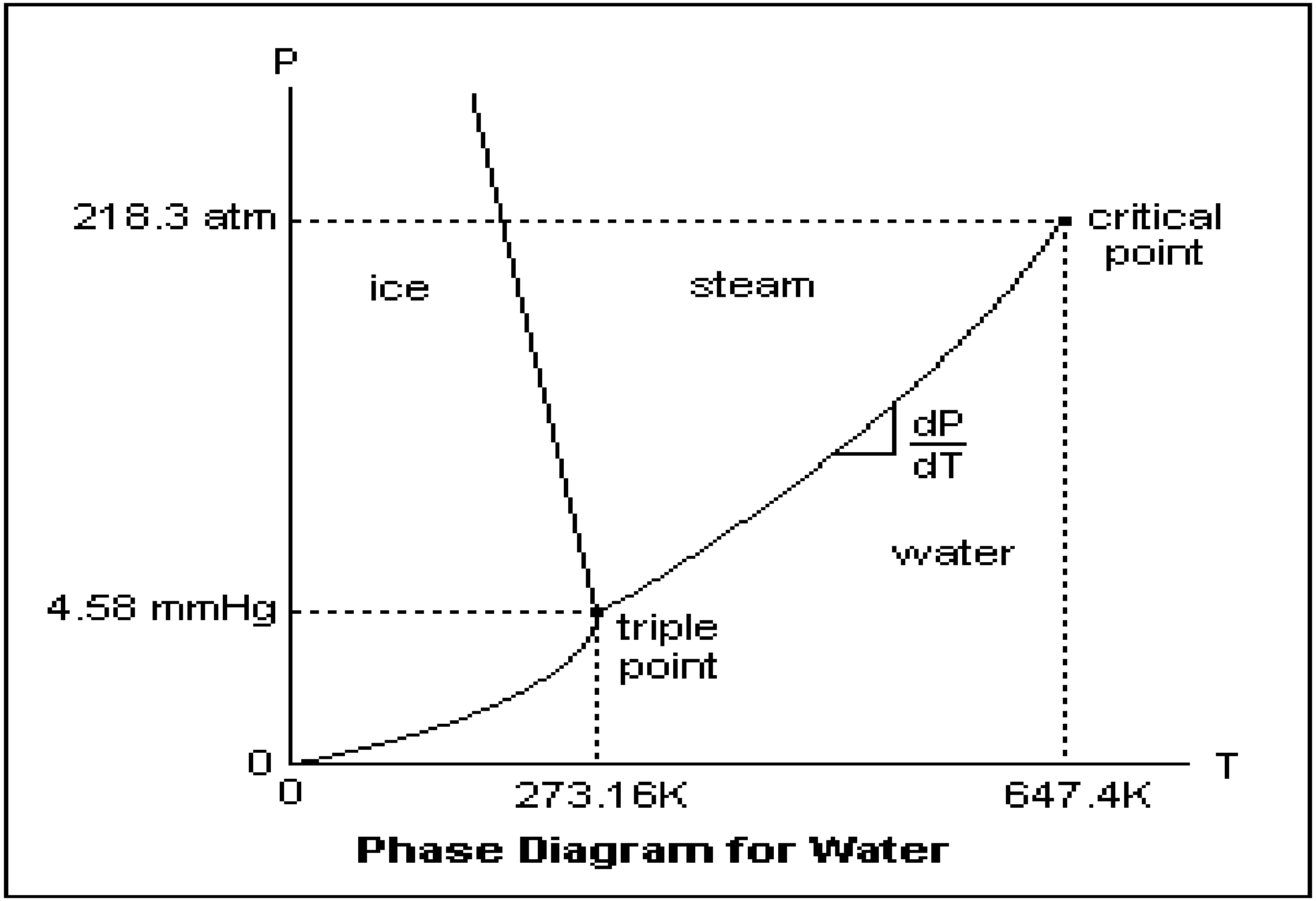
Ice

- When more heat is applied(absorbed), the hydrogen bonds(not the O-H bonds) break. The water molecules when first forming liquid cluster closer together.
- As they gain enough energy, they break free from the hydrogen bonding to become single molecules.

Chemical behavior of water

- Water is quite chemically stable.
- Require electric current for decomposition.

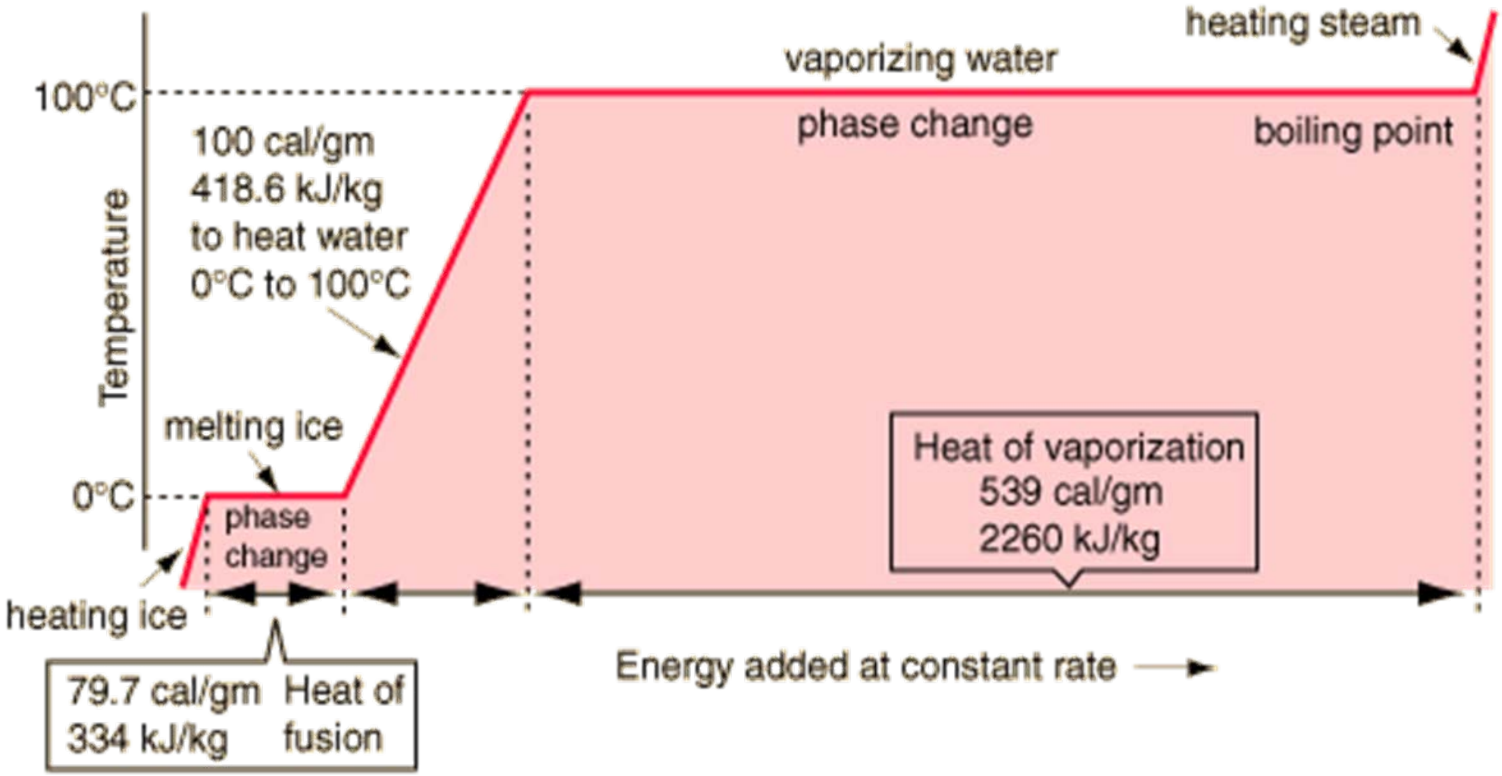
Phase diagram for water



Explanation of phase diagram

- This is the phase diagram of water. This shows the phases (solid, liquid & gas) of water according to pressure and temperature. At 4.58 mmHg and close to absolute zero water will be in all three phases at once. This is called **the triple point**.

Phase change diagram for dihydrogen monoxide



Phase change diagram

- This is a phase change diagram for water. The x-axis is energy and the Y-axis is temperature. The plateaus are the melting and boiling points.

Another look at water